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APPLICATION OF SELECTED METHOD FOR ASSESSMENT OF SELF-HEATING OF VEGETABLE OILS

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Research article

Abstract: One of the groups of materials that tend to self-combustion is vegetable oils. The amount of used oil used is currently increasing and thus the hazard of fires increases. For this reason, it is important to evaluate the tendency of oils for self-heating to minimize self-combustion. This article deals with assessment of the tendency of vegetable oils to self-combustion using two methods: Differential Mackey test and the method of thermal analysis. These methods evaluate the behaviour of oils during their heating. Thermal analysis using the Mettler-Toledo device was performed for oils without support and oils applied on the inert support. It was found that both methods are suitable for evaluation of the exothermic effect that occurs during oxidation of oils after their application on the solid supports. The obtained results of the analyses are the basis for mutual comparison of both way of measurement. Interpretation of these results is a contribution to increasing of safety during using oils.

Keywords: Self-heating; self-combustion; vegetable oils; Mackey test; thermal analysis.

Introduction

In food industry, vegetable oils are evaluated with respect to quality, behaviour during cooling and heating and oxidation resistance. Industrially, oils are used as a means of facilitating of yarn processing in the textile industry. In this application, oils are applied on fibrous solids, thereby conditions are created for self-heating of oils caused by oxidation. Then subsequent self-combustion may occur. During processing and using of oils in large quantities, oil leakage may occur. If there is contamination of the insulation materials, fire also may occur. As a result of the use of vegetable oils for technical purposes, including the production of lubricants and the production of biofuels, their oxidation resistance is one of the important features that, on the one hand, indicate the possibilities of their use, on the other, they determine safety precautions for their use.

Self-combustion of vegetable oils is a well-known cause of fires. Self-heating is due to autooxidation of the unsaturated double bonds of fatty acids, that are part of oil molecule. If the heat generated by autooxidation is not dissipated sufficiently into the surroundings, the temperature of material is continually increasing. When the ignition temperature of material is reached, self-combustion occurs. In connection with the tendency to self-heating, the behaviour of the oils during heating and their oxidation resistance are the most important parameters that are evaluated by various methods.

Some analytical methods are used for assessment of the tendency of oils to self-combustion. These methods determine predominantly the content of unsaturated fatty acids in the oils or the number of double bonds when heat is released during oxidation. These methods include, for example, method for determination of iodine number, peroxide index or chromatographic methods such as GC-MS.

The disadvantage of these methods is the fact that vegetable oils contain other substances that can influence their tendency to self-combustion. According to the publication (Baylon et al., 2008), these substance are natural or synthetic antioxidants that are added especially to edible oils to prevent their oxidation that to make worse their quality.

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These are, for example, citric acid, tocopherol (vitamin E), butylhydroxyanisole (E320), and so on. Therefore, methods that assess the thermodynamic properties of vegetable oils, without regard to their chemical composition, are more suitable.

One of the non-adiabatic methods is the Mackey test (Bowes, 1984). This method evaluates the tendency of oils to self-heating according to value of the temperature difference in the reference and sample chamber. The evaluated parameter is the difference between the temperature in the reference and sample chamber. Both chambers are heated to a constant temperature simultaneously. The higher the difference, the higher tendency of the evaluated oil to self-heating. During the test, the oil is applied on the cotton gauze in a weight ratio of 2: 1 (ASTM D 3523-92, 2007).

Some methods of thermal analysis are often used to assess the tendency to self-heating. Thermal analysis involves a number of methods by which a change of state of the tested material is studied depending on one of its physical properties, whereas the material is heated according to a predetermined program. At present, there are several dozen thermoanalytical methods that vary according to the evaluated physical property.

Thermal analysis is used to observe of the development or absorption of heat or the change in mass of a substance exposed to ambient temperature, which is increased by preselected rate, usually constant. Temperature changes are usually observed differentially in comparison to the behaviour of an inert sample of the same size, shape and physical properties that is simultaneously exposed to the same temperature increase.

Heat changes can be measured either on a base of the temperature changes that occur between the reactive and inert sample of material (Differential Thermal Analysis - DTA) or on a base of differences in electricity supplied to the heater of samples. The heater is necessary to achieve the same temperature in the reaction and inert sample at the whole selected program (Differential Scanning Calorimetry - DSC). Both techniques can be used simultaneously or individually with observations of mass changes (thermogravimetric analysis - TGA).

The advantage of thermal analysis is that it does not require chemicals and time-consuming procedures during preparation of measurement. In Differential Thermal Analysis (DTA), the evaluated parameter is the temperature difference between the sample and the reference material at the programmed temperature increase. The temperature range of measurement is from temperature of ambient to 1000 °C. In analysis of organic substances, it is often sufficient to keep the upper limit around 500-700 °C. The method is mainly used for the evaluation of phase changes of solids, for example alloys. This method can also be used for evaluation of the exothermic and endothermic effects that occur during heating of organic matter.

If the weight of the sample is the evaluated parameter depending on the programmed controlled temperature, the method is referred to as thermogravimetry (TG). From the magnitude of the weight changes and the corresponding temperature intervals, the composition of the sample or the quantitative representation of some of the components in the sample can also be judged.

The aim of this work is to compare the results obtained by Mackey test with results of iodine number and thermal analysis DTA and TG and to evaluate the applicability of these methods for oils self-combustion assessment.

Methods of thermal analysis used to evaluate the oxidative stability of oils

Baylon et al. (2008) informs about the use of the thermal analysis for the evaluation of the tendency of oils to self-combustion. Determination of oil composition and the ratio of saturated bonds to unsaturated or determination of iodine number is not considered sufficient to evaluate the degree of tendency of the oil to self-combustion. As a suitable method, Baylon et al. (2008) consider the non-isothermal DSC. By this method, oils and oils with antioxidant agents were tested in an inert atmosphere or in the air.

Coni et al. (2004) used a thermogravimetric method to determine the resistance of vegetable oils to oxidation. They determine the weight increase due to oxidation and the initial and final oxidation temperature. For this purpose, the method is considered to be adequate and bringing advantages against previously used methods.

Dweck and Sampaio (Dweck and Sampaio, 2004) used the thermogravimetric method in combination with differential thermal analysis DTA to analyse thermal decomposition of oils in the air and to determine their resistance to heating. Tested samples have shown a significant dependence between the combustion heat and the extrapolated initial decomposition temperature of the oils in the air.

The TGA method in combination with DSC was used to evaluate the temperature and oxidation properties of coconut oil in terms of its use as a base oil for industrial lubricants (Jayadas

and Prabhakaran, 2006). A low weight increase in the oxidizing environment is considered to be an indicator of the oxidative stability of coconut oil.

For evaluation of the oxidative properties of vegetable oils in terms of their use as a base oil for industrial lubricants, other methods have also been used (Jayadas and Prabhakaran, 2006). FTIR and NMR spectroscopy were used to quickly determinate the degree of unsaturation. The TGA method in combination with DTA in isothermal mode was used to evaluate the oxidation properties. The results of the TGA / DTA tests confirmed that polyunsaturated oils have lower oxidation stability than monounsaturated oils. However, in their opinion, the FTIR method is not well suitable for distinction of the oxidative resistance of oils.

Differential Compensation Calorimetry (DSC) is a well-known calorimetric technique that is recognized as a valuable tool for characterizing of the thermal behaviour of oils and fats. The advantage of this method is that it does not require chemicals or time-consuming procedures during preparation of measurements. Thermal parameters have a satisfactory correlation to chemical parameters related to the composition and oxidative stability of vegetable oils (Tan and Cheman, 2000; Tan et al., 2002).

According to study (Chiavaro et al., 2011), this method (DSC) is also able to evaluate the changes that occur due to microwave heating of oils. (Chiavaro et al, 2010) deals with the correlation between the thermal properties and the chemical composition of several types of olive oil. Olive oil is appreciated as a part of a healthy nutrition because it contains a high proportion of oleic acid (C18:1) and natural antioxidants, especially phenolic compounds. Thermal properties were evaluated by DSC.

Thermoanalytical methods are also used to study the thermal decomposition of commercially available oils (Santos et al., 2004). In addition to the DSC method, he also used TG and DTG methods. Classical differential thermal analysis and thermogravimetry were used to evaluate the influence of the type of support on the thermal stability of vegetable oils (Veznikova and Vanasek, 2006). Thermogravimer method and DTG were used to evaluate the process of thermal decomposition of triacylglycerols contained in olive oil (Vecchio et al, 2008). Thermogravimetry (TG), Differential Thermogravimetry (DTG) and Differential Thermal Analysis (DTA) were used to evaluate the resistance of vegetable oils to oxidation (Wesolowski and Erecinska, 1998).

The analysis shows that thermal analysis methods are used to evaluate the thermodynamic behaviour of oils, mainly to evaluate their oxidative stability. This property is important for assessment of the quality of edible oils, but it also determines the tendency of oils to self-combustion.

When the oils are applied on the solid, fibrous or porous support, they have a substantially enlarged surface and their exothermic reactions with oxygen lead to temperature increase. Under suitable conditions, this behaviour can lead to a fire.

Materials and methods

Commercially available vegetable oils were selected for evaluation: two kinds of sunflower oil, rapeseed oil, olive oil and one species food oil.

For these oils, determination of iodine number was performed by the standard method (ČSN 588761, 1995). The method assesses the tendency to self-combustion based on the chemical composition of oils. The method is based on the idea that the reactivity of the substance to oxygen depends on the content of the double bonds which are attacked by the oxidizing agents. The method of determination of the iodine number is contained in a number of normative documents relating to the quality of vegetable oils. It is considered to be an adequate method for assessment oils, especially in connection with the production of biofuels and with an assessment of their properties and properties of feedstocks. The iodine number or iodine index is the mass of iodine in grams that is consumed by 100 g of tested materials, more precisely, the mass of iodine, which reacts with double bonds in tested materials, under the test conditions. The iodine number is therefore an indicator of the amount of unsaturated fatty acids in the fats or oils.

The tendency of self-combustion of oils was evaluated by the differential Mackey test mentioned in ASTM D 3523-92 (2007). The method is designed for qualitative assessment of the tendency to self-heating of liquids and solids when these materials are exposed to air at the test temperature. It is applicable for testing of liquids and solids applied on the cellulose surface. It is not suitable for evaluation of self-heating of materials on metal or surfaces contaminated by metals.

The method is not intended to obtain quantitative evaluation, such as determination of the enthalpy of the sample reaction with air; this data can be obtained using an adiabatic calorimeter. The positive difference between the sample temperature during the experiment and the reference temperature is evidence of the thermochemical

reaction in the sample. If the difference between the sample temperature and the reference temperature is negative, it can not be excluded that the self-heating occurs when the tested oil is exposed to a higher temperature than the test temperature.

The principle of this empirical test is to measure the temperature in a test specimen prepared from 20 g of cotton gauze. 10 g of the tested oil is applied on gauze and it is placed in a cylindrical basket of wire mesh. The gauze is rolled into a cylinder. The thermocouple is placed at the centre of the gauze. The device has two chambers heated by a double casing. The gauze with a sample is in one chamber. The gauze without a sample is in the second, reference chamber, which is identical to the sample one. The result, called "value of the spontaneous heating (SHV)", is determined as the difference between the maximum temperatures in both chambers. The higher the value of this indicator, the higher the tendency of the self-combustion of tested liquid. If self-heating does not occur, the SHV is near zero. A more detailed description of the device and methods is given in (Veznikova, 2009).

Thermal analysis using the Mettler-Toledo device was performed on all materials in two ways. First, oil without support was inserted in the test cup. For the oxygen from the atmosphere, only the surface of the liquid was available in this arrangement. In a second method, a mixture of 20 mg of oil and 60 mg of powdered aluminium oxide was placed into the test cup. This inert material served as the support and provided an increase of the size of the oil surface that was accessible for oxygen. For analysis, the TG method in combination with DTA was used.

The programmed temperature rise during the analysis was determined as follows (table 1):

Tab. 1. Set temperature program

Temperature range [°C]	Temperature rise [°C/min]
25-120	25.0
120-500	2.5
500-800	50.0

Results and discussion

The results of determination of the iodine number are shown in table 2. According to the iodine value, sunflower oil contains the highest amount of double bonds. As expected, olive oil has the lowest value of the iodine number. The iodine number of rapeseed oil is approximately in the middle of the measured values. This division into three groups corresponds to the content of unsaturated acids in vegetable oils, determined by full analytical methods. Olive oil has only about 8% of this acid and contains about 70% oleic acid (18:1). Rape oil has mean linoleic acid content around 20-25% and besides, more than ten times linolenic acid (18:3) than other oils (Christie, 2011).

The results of the determination of SHV by Mackey test are listed in table 2. The higher the value of SHV, the higher the tendency of the tested oil to self-combustion. The negative value of SHV means that self-heating was not recorded in the sample. The determination was carried out using water as a heating liquid so that the bath temperature was close to the boiling point of the water (97-100 °C).

Tab. 2. Results of determination of iodine number and value of the spontaneous heating (SHV) by Mackey test

	Type of oil	Iodine number	SHV [°C]
1	CERESOL, One species food oil	124	-0.75
2	LUKANA, Sunflower oil	132	14.5
3	KAROLINA, Sunflower oil refined	129	38.2
4	KAROLINA, Rapeseed oil refined	108	-0.35
5	CARBONELL, Extra virgin olive oil	83	11.35

The results of the thermal analysis show that the oils applied on the inert support have a lower thermal stability than the oils without support. This demonstrate the positive effect of the support on ongoing, especially oxidation reactions. The weight rise due to oxidation was recorded at the start of the test for all oils. For oils on the support, this weight rise was from 2 to 4%. In the next stages of thermal decomposition, the oxidation of oils on the substrate was also more pronounced against oil without support. For carbonless substrate analyses, their carbonization was observed. Oils on the substrate did not carbonize or carbonized very little during heating. Given that all analysed materials are a mixture of chemical compounds, weight loss occurred in several phases, usually in three phases.

As example is given record from the TG-DTA analysis of sample 3 (Karolina, Sunflower oil) - see Fig. 1.

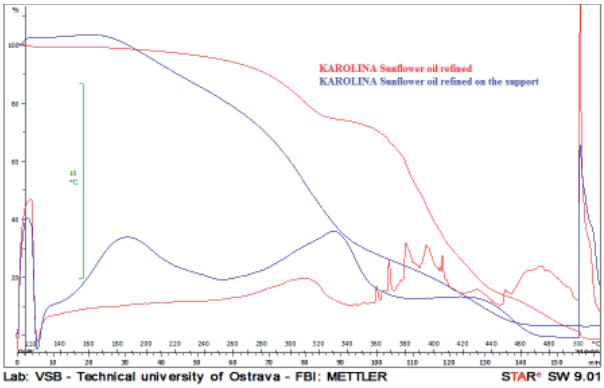

Fig. 1. Record from DTA analysis

The DTA curve clearly shows the first maximum which occurs for the oil on the support at a much lower temperature than in the case of the test of the oil without support.

The TG curve of oils without support shows weight loss, probably due to evaporation of volatile components, while weight gain due to oxidation is evident for oils on the substrate, at temperatures up to 200 °C.

In the next phase at a temperature above 345 °C, another accelerated weight decrease was recorded, approximately to the temperature about 450 °C. At this stage of the analysis, further decomposition and formation of carbonaceous residues occurred. By oxidation of carbonaceous residues the analysis is completed. In some cases up to temperature 500 °C, the weight of the sample dropped to zero. In others cases, the carbonaceous residue was oxidized even at a further temperature rise. All the materials decomposed without rest to temperature 800 °C (it is the maximum temperature in the selected temperature program).

Samples for analysis of oils on the support were prepared by blending oil and powdered Al_2O_3 in a weight ratio of 1:3 (20 mg oil and 60 mg Al_2O_3). The comparison determined that oils on the substrate have significantly greater the tendency to oxidation than oils without support. Oxygen binding already occurs at temperatures below 120 °C. This results in weight increase of sample. As the temperature rises, the weight of the samples slowly increases to about 170 °C.

The decomposition of the material took place in three phases. In the first phase, the decomposition of the individual oils varied considerably. The end of this phase fall to temperatures from 235 to 260 °C. The second and third stages of decomposition were very similar for all materials: the maximum loss. Maximum of weight loss rates are at the temperature around 310 °C (second phase), respectively, 430 °C (third phase). Maximum of heat development is mostly around the temperature 330 °C in the second phase and around 430 °C in the third phase. The lack of signification of these exoeffects in the third phase has to be attributed to the fact that the heat released by the oxidation of only several milligrams of oil heats up 60 mg Al_2O_3. All materials decomposed without rest to the temperature 460 °C, though recording of the mass did not drop to zero for most analyses.

The reactions associated with oxidation are manifested by the heat development. By DTA method, the temperatures at which the generation of heat is maximum, were determined. The comparison of the first maximums for oils and oils on the support is given in table 3. Temperatures, at which the maximums of temperature increase were found, were significantly higher for oils than oils applied on the support. In the case of liquid oil, oxidation can take place only on the surface of the liquid. For oil on the support, the oxygen penetrates to oil on the surface of the support easier and the oxidation, that manifests itself in exothermic effect, reaches the maximum at lower temperatures. The difference between these maximums can only be attributed to oxidation. These differences are given in table 3.

Tab. 3. Comparison of temperature maximum for oils and oils on the support

	Type of oil	Oil [°C]	Oil on the support [°C]	Difference [°C]
1	CERESOL, One species food oil	275	195	80
2	LUKANA, Sunflower oil	282	180	102
3	KAROLINA, Sunflower oil refined	311	130	181
4	KAROLINA, Rapeseed oil refined	319	210	109
5	CARBONELL, Extra virgin olive oil	326	205	121

The correlation coefficient between the iodine number and the result of Mackey test is 0.3124. The dependence between these two parameters, which are used to assess the tendency to self-combustion, respectively to assess the oxidative stability of oils, is therefore very small. This is a consequence of the presence of natural or added antioxidants that inhibit oxidation by reaction with free radicals. Determination of iodine number

method is not able to evaluate their inhibition effect and this is a great disadvantage of this method.

The coefficient of correlation between the difference in temperature of the first exothermic maximums found in oils and oils on the inert support and the results of Mackey test is 0.9150. This means that there is a strong dependence between the result of Mackey test and the value found as described from results of DTA.

Both methods are suitable for evaluation of exothermic effect which occurs during oil oxidation in the case of its application on the support. In this way, the oxidative stability of oils and their tendency to self-heating can be evaluated.

The methods of thermal analysis, as it appears from done the literature review, are often used to assess the tendency of oils to self-combustion or to assess their oxidative stability with regard to the quality of edible vegetable oils. The used device is more complex; however it allows to monitor in addition to thermal effects also kinetic parameters. Utilisation of the DSC method expands the temperature range at which the assessment is conducted toward lower temperatures. This is clearly an advantage for study oxidative effects that begin to run at normal ambient temperatures.

The method of differential Mackey test uses a simple device. Also, the determination of value of spontaneous heating (SHV) is simple. This method is sometimes referred to as time consuming and less accurate because of the asymmetry during application of oil on gauze used as the support (Baylon et al., 2008). On the other hand, the evaluation is performed on a defined shape of the sample, i.e. a cylindrical roll of gauze and with a larger quantity of the evaluated oil. The number of samples and their geometric configuration are very important for the course of self-heating. Therefore, it is possible to use this device for further study of the course of self-heating, for example using other materials of the support.

Conclusion

The comparison of the results confirmed that more suitable methods for assessment of the tendency to self-combustion are those that assess the thermal properties of oils during thermal oxidation than the methods that assess the chemical composition of oils, especially with regard to the number of double bonds. For the evaluation of oil in terms of tendency to self-heating, the oil applied on the solid support, which must be powdered or porous so that oxygen can penetrate to the surface of the oil on this support.

Two methods, the method of differential Mackey Test method and the TG method in combination with DTA, were used for evaluation. The results of both methods show mutual correlation. These methods are able to evaluate the tendency of oils to self-combustion in line with the behaviour of oils under realistic conditions. Therefore, both methods are suitable for assessment of the tendency of liquids with similar composition to self-combustion.

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